Vol. **114** (2008) *ACTA PHYSICA POLONICA A* No. 6–A

Optical and Acoustical Methods in Science and Technology

Heat Capacity and Internal Pressure of Cyclopentanol at Pressures up to 100 MPa Determined by the Acoustic Method

M. Dzida

Institute of Chemistry, University of Silesia, Szkolna 9, 40-006 Katowice, Poland

Isobaric heat capacities and internal pressures of cyclopentanol at pressures up to 100 MPa and temperatures ranging from 293 to 318 K were determined by the acoustic method. The obtained results were compared with those of pentan-1-ol in order to study the influence of the molecular configurations comprising cyclic and normal-chain structures on pressure and temperature dependence of the thermodynamic properties. It was found that the temperature and pressure coefficients of internal pressure were sensitive to the structural organization of the liquid and reflected the character of the interactions.

PACS numbers: 82.30.Rs, 62.50.–p, 65.40.Ba

1. Introduction

The thermodynamic properties of pentan-1-ol, 2-methyl-1-butanol and 2-methyl-2-butanol under pressures up to 100 MPa have been investigated previously [1, 2]. It was found that the pressure dependences of the heat capacity and internal pressure of the mentioned above alcohols show both similarities and differences. In the present work, the effect of the cyclic structure of the alcohol on the pressure dependence of those quantities has been examined as an extension of the previous investigations. With this end in view, cyclopentanol has been chosen. The heat capacities and internal pressures have been calculated using experimental speeds of sound measured within the temperatures from 293 to 318 K and at pressures up to 101 MPa together with the densities and heat capacities at 0.1 MPa [2]. The obtained results were compared with those of pentan-1-ol in order to study the influence of the molecular configurations comprising cyclic and normal-chain structures on pressure and temperature dependence of the thermodynamic properties. The association constant of cyclopentanol is identical to that of pentan-1-ol [3, 4]. The molar enthalpy of vaporization and the normal

boiling point of cyclopentanol is somewhat higher than that of pentan-1-ol [3, 5]. The relation between boiling points has been explained taking into account the "hot end" effects [5], i.e. the differences in the mobility of the end fragments of the molecules which affects their interactions. The rotation in cyclopentanol is restricted more than in pentan-1-ol which is sufficiently long to be bent. Kabo et al. [6] assumed that intramolecular degrees of freedom such as pseudorotation and internal rotation of hydroxyl group have rather high potential barrier in liquid cyclopentanol. Moreover, a low entropy difference between liquid and rigid crystal of cyclopentanol in comparison with other cyclopentane derivatives shows a relatively high degree of order in liquid [6]. This corresponds to the low heat capacity of cyclopentanol in comparison with other pentanols [7]. Moreover, the density of cyclopentanol is relatively high in comparison with other pentanols [7]. This indicates a close-packed structure of this alcohol. In this work the possible explanations of the similarities and differences between the pressure and temperature dependence of isobaric heat capacity and internal pressure of cyclopentanol in comparison with those of pentan-1-ol are proposed.

2. Experimental

Cyclopentanol from Fluka (purity $\geq$ 99% GC) were used. It was dried over 0.3 nm molecular sieves. The mass concentration of water, determined by the Karl Fischer method, was 0.02%. Each sample was degassed in an ultrasonic cleaner just before the measurement.

The speed of sound in liquid under test has been measured at temperatures from 293 to 318 K in about 5 K intervals at atmospheric and higher pressures up to 101 MPa using two measuring sets designed and constructed in our laboratory [8, 9]. The uncertainty of the speed of sound measurements was estimated to be better than ± 0.5 m s^{-1} at atmospheric pressure, and ± 1 m s^{-1} under higher pressures. Other details of the high-pressure device and the method of the speed of sound measurements can be found in the previous papers [8, 9].

The densities under atmospheric pressure were measured in the temperature range as above using a vibrating tube densimeter Anton Paar DMA 5000. The uncertainty of the density measurements was 0.05 kg m^{-3}, whereas the repeatability was estimated to be better than 0.005 kg m^{-3}.

3. Calculation of isobaric heat capacity and internal pressure under elevated pressures

The isobaric heat capacity and internal pressure were calculated by the acoustic method. In calculations the measured speeds of sound as function of temperature and pressure together with densities as function of temperature under atmospheric pressure and the literature isobaric heat capacities for the atmospheric pressure were used. The temperature dependence of the isobaric heat capacity at atmospheric pressure reported by Zábranský et al. [10] was applied.

The method, based on the suggestion of Davis and Gordon [11] with a numerical procedure proposed by Sun et al. [12] slightly modified by Marczak et al. [13] was applied. Finally, the procedure gives the isobars of density and heat capacity in the form of the second order polynomial of temperature. Details of the algorithm were discussed in previous works [13, 14]. From the experimental speeds of sound, calculated densities and heat capacities, the internal pressures, p_{int}, were obtained in the following way:

$$p_{\mathrm{int}} = \left[T\alpha_p \left(\frac{1}{\rho u^2} + \frac{\alpha_p^2 T}{\rho C_p} \right)^{-1} \right] - p, \tag{1}$$

where α_p is the isobaric thermal expansion, ρ is density, u is the speed of sound, C_p is the specific heat capacity. The idea of internal pressure and the method of obtaining of Eq. (1) was described in detail in the previous work [15].

4. Results and discussion

The isobaric heat capacity and internal pressure of cyclopentanol were calculated for temperatures from 293.15 to 318.15 K and for pressures up to 100 MPa. The results are plotted in Figs. 1 and 2a. The effect of pressure on isobaric heat capacity (Fig. 1) and pressure dependence of internal pressure (Fig. 2) of cyclopentanol and pentan-1-ol are similar. It suggests that the effect of pressure on association is probably similar to each other. The molar heat capacity slightly decreases with increasing pressure. The internal pressure of cyclopentanol and pentan-1-ol as function of pressure shows a maximum, i.e. the internal pressure first increases with increasing pressure and then it decreases. With increasing temperature the maximum moves toward higher pressures. However, the temperature dependences are different for each of the alcohols investigated. For pentan-1-ol a crossing point of the internal pressure isotherms exists. The internal pressure decreases with increasing temperature at pressures up to the crossing point and than it increases with the increase in temperature. For cyclopentanol this crossing point is not observed, and the internal pressure increases with increasing temperature over the whole investigated pressure range.

Kartsev et al. [16–19] noticed that under atmospheric pressure the temperature coefficient of internal pressure is sensitive to the structural organization of the liquid and reflects the character of the interactions. According to the sign of the temperature coefficient of the internal pressure, liquids can be classified as: (a) not hydrogen-bonded for which the temperature coefficient of the internal pressure is smaller than zero; (b) hydrogen-bonded with spatial net of H-bonds for which the temperature coefficient of the internal pressure is greater than zero; (c) associated which characterized inversion of the temperature coefficient of the internal pressure; sign reversal from (+) to (–). They showed that linear alkan-1-ols are characterized by the inversion of the temperature dependence of p_{int}. The internal pressure of pentan-1-ol decreases very slightly with increasing temperature

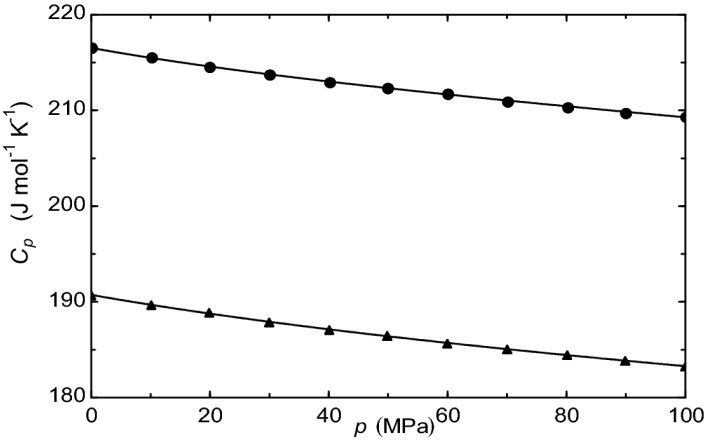

Fig. 1. Molar heat capacities of: (▲) cyclopentanol and (●) pentan-1-ol [1] as function of pressure at 308.15 K.

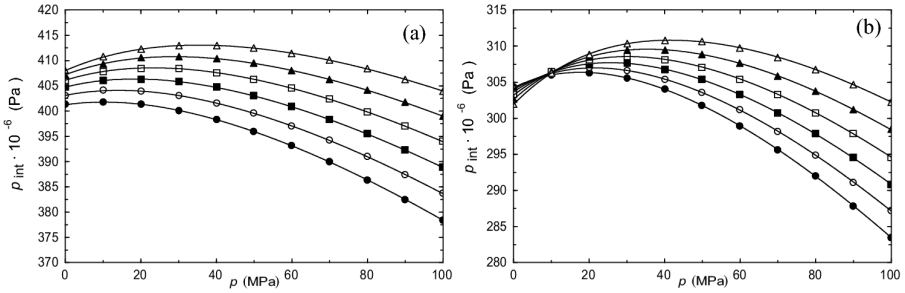

Fig. 2. Pressure dependence of internal pressure of (a) cyclopentanol and (b) pentan--1-ol at • 293.15 K; ○ 298.15 K; ■ 303.15 K; □ 308.15 K; ▲ 313.15 K; △ 318.15 K.

at temperatures 293.15 and 298.15 K under atmospheric pressure and at 303.15 K the effect of temperature on p_{int} becomes most pronounced. It is surprising that the temperature dependence of internal pressure of cyclopentanol is similar to that of diols [20–22]. Temperature and pressure dependences of the internal pressure of cyclopentanol is very similar to those of propano-1,2-diol [20]. Propano-1,2-diol is able to form spatial net of H-bonds and moreover intramolecular H-bonds which results in five-membered rings. Rappon and Lin [23] studied properties of cyclohexanol + heptane binary mixtures. They suggested that in these mixtures cyclohexanol formed cyclic multimers which would facilitate the formation of hydrogen bonding between rings by the use of bifurcated H-bonds. If cyclopentanol could form similar associates in pure state, it would partially explain similarities between cyclopentanol and diols.

5. Conclusions

Pressure dependence of the isobaric heat capacity and internal pressure qualitatively confirm similarities and dissimilarities of physicochemical properties of cyclopentanol and pentan-1-ol. Basing on the results obtained in this work and previous research [1, 15, 20–23], it is possible to find correlations between the temperature and pressure dependence of internal pressure and molecular interactions and structure of alcohols, and also for diols. The crossing point of the isotherms of internal pressure under relatively low pressure is characteristic of linear alkan-1-ols, and diols for which the formation of intramolecular hydrogen bonds is somewhat restricted on steric groups. The pressure and temperature where p_{int} is maximum can be connected with the ability to self-association of alcohols or ability to form the intramolecular hydrogen bonds in case of diols. Sometimes both temperature and pressure dependence of internal pressure confirm similarities and/or differences between two compounds, as in case of cyclopentanol and propano-1,2-diol. The results obtained are very promising but need additional confirmation, in particular examination of more systems with other functional groups in the molecules and different structures.

References

[1] M. Dzida, *Eur. Phys. J. Special Topics* **154**, 271 (2008).

[2] M. Dzida, *J. Chem. Eng. Data*, 2008, submitted for publication.

[3] H. Kaur, N.S. Samra, B.S. Mahl, J.R. Khurma, M. Bender, A. Heintz, *Fluid Phase Equilib.* **67**, 241 (1991).

[4] D. Kulikov, S.P. Verevkin, A. Heintz, *Fluid Phase Equilib.* **192**, 187 (2001).

[5] I.B. Golovanov, S.M. Zhenodarova, *Russ. J. Gen. Chem.* **75**, 1904 (2005).

[6] G.J. Kabo, V.V. Diky, A.A. Kozyro, A.P. Krasulin, V.M. Sevruk, *J. Chem. Thermodyn.* **27**, 953 (1995).

[7] G.C. Benson, P.J. D'arcy, *J. Chem. Thermodyn.* **18**, 493 (1986).

[8] A. Żak, M. Dzida, M. Zorębski, S. Ernst, *Rev. Sci. Instrum.* **71**, 1756 (2000).

[9] M. Dzida, M. Chorążewski, M. Zorębski, R. Mańka, *J. Phys. IV (France)* **137**, 203 (2006).

[10] M. Zábranský, V. Růžička, E.S. Domalski, *J. Phys. Chem. Ref. Data* **30**, 1199 (2002).

[11] L.A. Davis, R.B. Gordon, *J. Chem. Phys.* **46**, 2650 (1967).

[12] T.F. Sun, C.A. Ten Seldam, P.J. Kortbeek, N.J. Trappeniers, S.N. Biswas, *Phys. Chem. Liq.* **18**, 107 (1988).

[13] W. Marczak, M. Dzida, S. Ernst, *High Temp.-High Press.* **32**, 283 (2000).

[14] M. Dzida, *J. Sol. Chem.* **33**, 527 (2004).

[15] M. Dzida, *J. Chem. Eng. Data* **52**, 521 (2007).

[16] V.N. Kartsev, M.N. Rodnikova, I. Bartel, S.N. Shtykov, *Russian J. Phys. Chem.* **76**, 1016 (2002).

[17] V.N. Kartsev, M.N. Rodnikova, S.N. Shtykov, *J. Struct. Chem.* **45**, 91 (2004).
[18] V.N. Kartsev, M.N. Rodnikova, S.N. Shtykov, *J. Struct. Chem.* **45**, 96 (2004).
[19] V.N. Kartsev, *J. Struct. Chem.* **45**, 832 (2004).
[20] E. Zorębski, M. Piotrowska, M. Dzida, *Acta Phys. Pol. A* **114**, A–265 (2008).
[21] M. Cempa, M. Dzida, E. Zorębski, *Fortschritte der Akustik-DAGA* , 355 (2008).
[22] R.E. Gibson, O.H. Loeffler, *J. Am. Chem. Soc.* **63**, 898 (1941).
[23] M. Rappon, S.-W. Lin, *J. Mol. Liq.* **85**, 313 (2000).